SUBSTITUTION AND PROTONATION REACTIONS OF NITRILOTRIACETATOCRCHROMIUM(III) IONS

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Abstract—The reaction of NH₄[Cr(NTA)(H₂O)₆] (NTA = nitrilotriacetic acid) with H⁺ has been studied at different temperatures and a rate constant of 1.27(3) x 10⁻² s⁻¹ was obtained at 25.1°C. It is proposed that the reaction involves the formation of an ion pair, followed by the protonation of one of the carboxylate groups of the NTA ligand bonded to the central metal ion. This results in the formation of the [Cr($\eta$-NTA)(H₂O)₆]⁺ complex. The substitution reactions between [Cr(NTA)(H₂O)₆]/[Cr(NTA)(OH)(H₂O)]⁻ and different ligands (NCS⁻ and EBT⁻; EBT⁻ = Eriochrome Black T) were also studied. The second-order rate constant for the reaction of NCS⁻ with the [Cr(NTA)(H₂O)₆] complex at 35.0°C was 9.1(1) x 10⁻³ M⁻¹ s⁻¹ and that for the reaction of EBT⁻ with the metal complex at 30.0°C was 9.5(6) x 10⁻² M⁻¹ s⁻¹. The increase in substitution rate for the reaction between [Cr(NTA)(H₂O)₆] and EBT⁻ is attributed to the chelation of the EBT⁻ ligand during this reaction.

Chromium salts are extensively used as metallic mordants in the dyeing industry due to their positive effect on colourfastness and relative low cost. Residual chromium salts in effluents have, however, become an ecological problem and modifications to existing procedures and new colouring techniques are currently being developed.¹ ²

In most commercial processes chromium is applied by treating the wool with Cr₂O₃²⁻/CrO₄²⁻ solutions at approximately 100°C. During this process the chromium(VI) is reduced to chromium(III) by functional groups in the wool-like cysteine and tyrosine, or auxiliary reducing agents such as S₂O₅²⁻ and HSO₃⁻.³ ⁴ The chromium(III) ions then react via substitution reactions with both the colouring agent and the functional groups in the wool fibre to form the highly coloured complex attached to the wool fibre via the functional groups of the wool, giving it its colourfastness.

Kinetic studies involving chromium(III) have been extensively investigated and the principal characteristic of most of these results was the relative inertness of these complexes towards substitution reactions.⁵ ⁶ Recent studies, however, have shown that the reactivity of the chromium(III) ion can be improved by orders of magnitude if electron-donating ligands are bonded to the metal ion. Studies have shown that [Cr(TPPS)(H₂O)₆]³⁻ (the TPPS porphyrin is highly electron rich) reacts for example about 2500 times faster with NCS⁻ (k₁ = 4.7 x 10⁻³ M⁻¹ s⁻¹) compared with the reaction between [Cr(H₂O)₆]³⁺ and NCS⁻ (k₁ = 1.8 x 10⁻⁶ M⁻¹ s⁻¹).⁸

Another ligand which has the ability to increase
the reactivity of the chromium(III) ion is nitrito- 
triacetic acid (NTA). The NTA ligand acts as a 
tetradentate ligand, coordinating via a nitrogen and 
three oxygen atoms to the metal ion. The octahedral 
group of the ion is completed by two aqua 
ligands, which are cis bonded in the complex. These 
features (reactivity and cis aqua ligands) make this 
complex highly suitable to use as a model complex 
to study the reactions between chromium(III) and 
different ligands such as NCS" and colouring 
agents for wool like Eriochrome Black T (EBT), as 
well as to investigate its ability to react with wool 
 fibre in an attempt to find alternative chromium(III) 
mordants.

EXPERIMENTAL

NH₄[Cr(NTA)(OH)(H₂O)]·2H₂O was prepared 
using a method similar to that used by Uehara 
and co-workers. The precipitate was obtained by 
adding ethanol to solutions containing the final 
product. The UV–vis spectra were recorded and the 
reactions monitored on a Hitachi (model 150-20) 
double-beam spectrophotometer connected to a 
Fryka–Kalteknich KB 300-thermostated bath. IR 
spectra were recorded on a Hitachi (model 270-50) 
IR spectrophotometer. All pH measurements were 
performed on an Orion (model 701) pH meter, 
using potassium hydrogen phthalate and potassium 
dihydrogen phosphate/disodium hydrogen phos- 
phate as buffer solutions.

The kinetics were studied under pseudo-first- 
order conditions. Linear plots of log(A₀–A₁) vs time 
were obtained for at least two half-lives under all 
conditions. All measurements (except for EBT as a 
ligand) were performed at a constant ionic strength 
of 1.0 M (NaNO₃) after ensuring that the nitrate 
ions do not label the chromium complex. The 
rate and equilibrium constants were calculated with 
a 386-personal computer using a non-linear least- 
squares program.

RESULTS AND DISCUSSION

Reaction with H⁺

The [Cr(NTA)(H₂O)]⁺ (µK₄ = 5.47)³ complex 
was obtained by acidifying a [Cr(NTA)(OH) 
(H₂O)]⁺ solution. A slow change in the UV–vis 
spectra was observed at low pH values (pH < 1.0), 
which did not correspond to normal protonation 
reactions. Substitution reactions with different 
ligands (anions) at these pH values were elimi- 
nated by the study of the reactions between [Cr

<table>
<thead>
<tr>
<th>Reactant</th>
<th>(10³)k_{obs}</th>
<th>(s⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>0.2 M HCl</td>
<td>5.38(4)</td>
<td></td>
</tr>
<tr>
<td>0.2 M HCl+0.4 M NaCl</td>
<td>5.55(4)</td>
<td></td>
</tr>
<tr>
<td>0.2 M HClO₄</td>
<td>5.44(3)</td>
<td></td>
</tr>
<tr>
<td>0.4 M HCl</td>
<td>7.99(2)</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Observed rate constants for the reaction between [Cr(NTA)(H₂O)]⁺ and different acids and anions

Scheme 1.

Fig. 1. Plot of k_{obs} vs [H⁺], µ = 1.0 mol dm⁻³ and λ = 550 nm.
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Table 2. Summary of the rate and stability constants and activation parameters for the reactions between \([\text{Cr(NTA)}(\text{H}_2\text{O})_2]\) and various ligands

<table>
<thead>
<tr>
<th></th>
<th>(\text{H}^+)</th>
<th>(\text{NCS}^-)</th>
<th>(\text{EBT}^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Temperature (°C)})</td>
<td>15.4</td>
<td>25.1</td>
<td>35.0</td>
</tr>
<tr>
<td>((10^9)k_e^\dagger)</td>
<td>5.2(2)</td>
<td>12.7(3)</td>
<td>31.7(2)</td>
</tr>
<tr>
<td>((10^9)k_e^\ddagger)</td>
<td>1.25(8)</td>
<td>1.78(9)</td>
<td>3.8(2)</td>
</tr>
<tr>
<td>((10^9)k_{-2}^\gamma)</td>
<td>23.0(3)</td>
<td>10.3(3)</td>
<td></td>
</tr>
<tr>
<td>(K(M^{-1}))</td>
<td>3.7(4)</td>
<td>4.3(4)</td>
<td>2.6(4)</td>
</tr>
<tr>
<td>(\Delta H^\ddagger (\text{kJ mol}^{-1}))</td>
<td>65.9(5)</td>
<td>39(5)</td>
<td>74(2)</td>
</tr>
<tr>
<td>(\Delta S^\ddagger (\text{J mol}^{-1} \text{K}^{-1}))</td>
<td>-147(5)</td>
<td>-158(8)</td>
<td>-18.8(3)</td>
</tr>
</tbody>
</table>

\(a\) See Scheme 1.
\(b\) See Scheme 2.
\(c\) See Scheme 3.
\(d\) Equation (1).
\(e\) Equation (5).
\(f\) Equation (6).
\(g\) Equation (4).
\(h\) Equation (3).
\(i\) \(K_1 = k_1/k_{-1}\).

The substitution reaction between \([\text{Cr(NTA)}(\text{H}_2\text{O})_2]\) and \(\text{NCS}^-\) was studied at pH values between 3 and 6. At these pH values, where both chromium(III) species can react with \(\text{NCS}^-\), the following reaction scheme is proposed:

\[
\text{[Cr(NTA)(OH)(H}_2\text{O)}_2]^- + \text{NCS}^- \rightarrow \text{[Cr(NTA)(NCS)(OH)(H}_2\text{O)}_2]^- + \text{H}^+ + \text{H}_2\text{O}
\]

Scheme 2.

The stability constants of \([\text{Cr(NTA)(NCS)(H}_2\text{O)}_2]^-\) were determined spectrophotometrically at pH 3.6. At this pH the only chromium(III) species present are \([\text{Cr(NTA)}(\text{H}_2\text{O})_2]\) and \([\text{Cr(NTA)(NCS)(H}_2\text{O)}_2]^-\). From the definition of \(K\) (see reaction scheme), Beer's law and mass balance, eq. (3) can be derived

\[
A = (A_M + A_{ML}K_1[\text{NCS}^-])/(1 + K[\text{NCS}^-]).
\]

\(A\) is the absorbance at a given concentration of \(\text{NCS}^-\), \(A_M\) and \(A_{ML}\) are the absorbances of \([\text{Cr(NTA)}(\text{H}_2\text{O})_2]\) and \([\text{Cr(NTA)(NCS)(H}_2\text{O)}_2]^-\), respectively. The absorbance vs \([\text{NCS}^-]\) data were fitted to eq. (3) and the calculated \(K_1^-\) values are reported in Table 2.

According to the reaction scheme the observed pseudo-first-order rate constant is given by eq. (4):

\[
k_{obs} = [(k_1[H^+] + k_2K_{a1})/([H^+] + K_{a1})][\text{NCS}^-]
+ (k_{-1}[H^+] + k_{-2}K_{a2})/([H^+] + K_{a2}).
\]

Equation (4) simplifies at pH 3.6 to eq. (5):

\[
k_{obs} = k_1[\text{NCS}^-] + k_{-1}.
\]

Plots of \(k_{obs}\) vs \([\text{NCS}^-]\) data at pH 3.6 were linear (see Fig. 2) and the \(k_1\) and \(k_{-1}\) values were calculated using a non-linear least-squares program, see Table 2.
[Cr(NTA)(OH)(H$_2$O)$^-$] will, according to the reaction scheme (Scheme 2), increase with an increase in pH. The results in Fig. 3 clearly show an increase in substitution rate with an increase in pH. Precipitate formation at pH values greater than 5.9 prevented the study of these reactions at higher pH. The $k_2$ value was calculated from the slope of the plot of $k_{obs}$ vs [NCS$^-$] data at pH 5.85 using eq. (6). At this pH the slope of this plot is represented by eq. (6):

$\text{Slope} = \frac{K_{d2} + k_2 K_{a1}}{K_{d1} + K_{d2}}.$ (6)

The values of $k_{-2}$ and $K_{a2}$ were calculated by fitting the data in Fig. 3 (using $k_1$, $k_{-1}$, $k_2$ and $K_{a1}$ values already determined) to eq. (4). The results are presented in Table 2.

The second-order rate constant of $5.8 \times 10^{-3}$ M$^{-1}$ s$^{-1}$ at 25°C for the reaction between [Cr(NTA)(OH)(H$_2$O)]$^-$ and NCS$^-$ compares favourably with the $k_1$ value of $4.7 \times 10^{-3}$ M$^{-1}$ s$^{-1}$, which was obtained for the reaction between [Cr(TPPS)(H$_2$O)$_3$]$^-$ and NCS$^-$. This much smaller labilizing effect of the hydroxo ligand in the NTA ligand compared with TPPS may be attributed to the fact that the hydroxo and aqua ligands in [Cr(NTA)(OH)(H$_2$O)]$^-$ are cis-bonded to one another and it is well known that a cis effect is usually much smaller than a trans effect. The large negative $\Delta S$ value suggests an associative activation.

**Reaction with Eriochrome Black T**

The reaction between [Cr(NTA)(OH)(H$_2$O)]$^-$ and Eriochrome Black T (EBT) was also studied at pH between 3 and 6. The pH at which wool is usually coloured is in this range. Since the $pK_a$ value of [Cr(NTA)(H$_2$O)$_3$] and EBT are 5.47 and 6.3, respectively, there are two reactive chromium(III) species and two reactive EBT species present at this pH, see Scheme 3.

These reactions were performed with [Cr(NTA)(OH)(H$_2$O)$_3$] $\gg$ [EBT$^-$] due to the colour intensity of EBT$^-$ solutions to ensure pseudo-first-order conditions. In order to simplify the study, the reactions were first performed at pH 4.0. At this pH, [Cr(NTA)(OH)(H$_2$O)$_3$] and EBT$^-$ are the main species in the solution and the reaction scheme simplifies to eq. (7):

$$\text{[Cr(NTA)(H$_2$O)$_3$] + EBT$^-$ } \rightarrow \frac{k_1}{k_{-1}} \text{[Cr(NTA)(EBT)$^-$]}.$$ (7)

The reaction proceeds probably via two steps: one water molecule is substituted in the rate-determining step while the second water molecule is substituted during the fast and ring-closure step.

The stability constant of [Cr(NTA)(EBT)$^-$] was determined spectrophotometrically by fitting absorbance vs [Cr(NTA)(H$_2$O)$_3$] data to a modified
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An increase in substitution rate with an increase in pH, illustrating the cis labilizing effect of the hydroxo ligand. Precipitation formation at pH values greater than 5.7 prevented the complete study of these reactions at higher pH.

The reaction between \([\text{Cr(NTA)(H}_2\text{O)}_3]\) and EBT\(^{-}\) is about 16 times faster \((9.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1} \text{ at } 30^\circ\text{C})\) than the corresponding reaction between \([\text{Cr(NTA)(H}_2\text{O)}_3]\) and NCS\(^{-}\) \((5.8 \times 10^{-3} \text{ at } 25^\circ\text{C})\) and about 20 times faster than the reaction between \([\text{Cr(TPPS)(H}_2\text{O)}_2]^\text{-}\) and NCS\(^{-}\). This increase in substitution rate is attributed to the chelation of the EBT\(^{-}\) ligand during this reaction. The increase in substitution rate with an increase in pH is attributed to the cis labilizing effect of the hydroxo ligand in \([\text{Cr(NTA)(OH)(H}_2\text{O)}_2]^\text{-}\).

The increase in stability \((K_t = 180 \text{ M})\) of \([\text{Cr(NTA)(EBT)}^-\) compared with \([\text{Cr(NTA)(NCS)}(\text{H}_2\text{O)}_2])^-\ (K_t = 4.60)\) is also attributed to chelation.

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2. B. Kramrich, Wool Record, 35 (December 1986).

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**Fig. 4.** Plot of \(k_{\text{obs}}\) vs \([\text{Cr(NTA)(H}_2\text{O)}_3]\), pH = 4.0 and \(\lambda = 680 \text{ nm}\).

**Fig. 5.** Plot of \(k_{\text{obs}}\) vs pH at 35.0°C, \([\text{Cr(NTA)(H}_2\text{O)}_3]\) = 0.005 mol dm\(^{-3}\) and \(\lambda = 680 \text{ nm}\).